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An invited talk

Yue, Yuanzheng; Smedskjær, Morten Mattrup

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Controlling the Cationic Diffusion in Silicate Glasses

Yuanzheng Yue[1] and Morten M. Smedskjaer[2]

[1]Aalborg University, 9000 Aalborg, Denmark
[2]Corning Incorporated, Corning, NY 14831, USA

Over the past few years we have systematically studied the redox-driven diffusion in polyvalent element containing silicate glasses around T_g, and its impact on the glass surface structure and properties. Thermal oxidation induces outward diffusion (from interior to surface) of modifying ions and thereby formation of a crystalline surface layer enriched in alkali or alkaline earth oxides, whereas thermal reduction causes the cationic inward diffusion (from surface to interior) and hence formation of an amorphous surface layer enriched in silica. The crystalline surface layer enhances the high temperature stability of glass fibers. Even more importantly, the amorphous silica rich surface layer greatly enhances the chemical, mechanical, and thermal stability of glasses. Now the question arises: Is the inward diffusion reversible? In other words, can the inwardly diffused ions diffuse outward again, i.e., move back to the surface layer by subjecting the reduced glass to an oxidation process? To answer this question, we have performed the following experiments. First, an iron- containing diopside glass is treated under a reducing condition, and then the elemental concentration profiles of the surface layer are determined using secondary neutral mass spectroscopy (SNMS). After reduction, the reduced glass is re-treated, but under an oxidation condition this time, and then measured again using SNMS. Finally, we have found that the cation inward diffusion is indeed reversible in an appreciable quantity. This strongly confirms that the formation of the amorphous silica layer is solely caused by the inward diffusion of the modifying ions, particularly alkaline earth ions. This is also evidence that the silica rich layer is still glassy. If it was crystalline, the reversible motion of the alkaline earth ions would have been at least partly blocked. The hindrance of the crystal structure to the alkaline earth diffusion is verified by doing the opposite of the above mentioned experiment, i.e., oxidation-SNMS-reduction-SNMS. These results show that the Mg^{2+} ions in the crystalline surface layer of the oxidized glass do not move completely inward again when the glass is being reduced. This is due to the blocking role of the crystalline structure. These two types of experiments could provide information on the relation between the materials structure and the kinetic process. In addition, we have treated analogous iron-free glasses around T_g under both reducing and oxidizing conditions. The results show that these glasses do not exhibit any inward or outward diffusion. This is another evidence that the silica layer is indeed induced by inward diffusion, and thus not by evaporation of the alkaline earth ions into the surrounding atmosphere.

In summary, both the direction and the extent of the diffusion processes are controllable, and hence, the surface layers can be tailored regarding specific properties. Furthermore, we have revealed the kinetic and thermodynamic mechanisms of formation of both the crystalline and amorphous surface layers on the polyvalent element containing silicate glasses.